THE PHOTOCHEMICAL CONVERSION OF SOME HETEROCYCLIC ACRALDEHYDES INTO DERIVATIVES OF THE CORRESPONDING PROPIONIC ACIDS

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The few reports on the action of light on  $\alpha,\beta$ -unsaturated aldehydes commonly refer to 'polymer formation'. We have reported<sup>1,2</sup> the very ready cis  $\rightarrow$  trans isomerisation of the pyridotriazole acraldehydes (e.g. (1)  $\rightarrow$  (2)) and in an attempt to achieve the trans  $\rightarrow$  cis isomerisation we irradiated aldehyde (2) in various solvents. In methanolic solution (Hanovia medium pressure lamp, through quartz), after 1 hr., a 74% conversion into a single product was observed; this product which was also obtained by similar irradiation of the cis aldehyde (1) (85% after 1.5 hr.) was methyl 3-(3-pyridotriazolyl)-2methylpropionate (3), b.p. 132-138°/0.05 mm  $v_{max}^{film}$  1735 cm<sup>-1</sup>; n.m.r.  $\delta$ (CDCl<sub>3</sub>) 1.25 (3H, d), 2.7-3.4 (4H, m), 3.55 (3H, s) and 6.6-8.8 (4H, aromatic ring) p.p.m. That this reaction was not general for 3-arylacraldehydes was shown by its failure with cinnamaldehyde (polymer formation through quartz, trans-cis isomerisation through Pyrex), or 2-furylacraldehyde (polymer formation). We suspected that the adjacent nitrogen lone pair played a crucial part in the photochemical conversion; this suspicion was further strengthened by the observation that of the three isomers (4), (5) and (6), only 2-pyridylacraldehyde (4) was converted into methyl

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2-pyridylpropionate (7), albeit in poor yield (the ester (7) was identical with a sample obtained by catalytic hydrogenation of methyl 2-pyridylacrylate). The 3- and the 4-pyridylacraldehydes gave a mixture of polymeric material and the corresponding cis-acraldehydes on irradiation in methanol. The nitrogen lone pair was further implicated in the photochemical reaction by the observation that irradiation of 2-pyridylacraldehyde (4) in aqueous sulphuric acid gave no 2-pyridylpropionic acid, the product in this case, m.p.  $145-146^{\circ}$ , having formula  $C_{\rm o}H_{\rm o}NO_2$  of undetermined structure.



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For more detailed study of the reaction the most suitable compound was found to be the v-triazolylacraldehyde (8), <sup>3</sup> obtainable only in the trans-form. The acraldehyde (8) was converted in virtually quantitative yield after 1 hr. in methanol (medium pressure lamp, through quartz) to methyl 3-(4 v-triazolyl) propionate, (9), m.p. 65-66 v<sup>CHC1</sup><sub>max</sub> 1719 cm<sup>-1</sup>; n.m.r.  $\delta$ (CDC1<sub>3</sub>) 2.6-3.2 (4H, m), 3.65 (3H, s) 4.02 (3H, s) and 7.35 (1H, s) p.p.m. Irradiation in aqueous media gave the propionic acid (10), m.p. 150-152° (28% conversion after 1 hr.). Surprisingly, the irradiation in 20% sulphuric acid (in which the triazole (8) was shown to be protonated by a study of its u.v. absorption) gave the protonated acid (10) although at a considerably reduced rate (16% after 1 hr.). It is not clearly established whether the protonation of the triazole proceeds exclusively at nitrogen atom 3, or if there is an equilibrium protonation of atoms 2 and 3 with some lone pair residual at position 3. However, the quaternary salt (11) gave no trace of saturated ester when irradiated in methanol and we feel that participation of the lone pair on the nitrogen atom adjacent to the unsaturated side chain is clearly established. At this stage we suggest the mechanism shown in the SCHEME.

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A test of this proposal is provided by two experiments with deuterium labelled reagents. First, the dideuterated triazolo-pyridylacraldehyde  $(12)^2$  was irradiated in normal methanol; the isolated ester (13) was found to have one deuterium atom only, at carbon atom 3 (n.m.r. integration and mass spectrum). Secondly the v-triazolylacraldehyde (8) was irradiated in CH<sub>3</sub>OD; the isolated ester (14) had one deuterium atom at carbon 3 and one at carbon 2 as required by the mechanism proposed above.

Further work is in progress to prove the intermediacy of the ketene, and to establish the photochemical intermediate (15) in the reaction; at the moment it seems plausible to formulate the intermediate (15) with a cis geometry and to suggest that it has diradical character with an electron deficient N3 which abstracts the aldehyde proton to give the ketene.

## REFERENCES

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